

Thermally activated barrier crossing and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential

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Abstract

We study the stochastic resonance (SR) of a flexible polymer chain crossing over a piecewise linear bistable potential. The dependence of signal to noise ratio SNR on noise intensity D , coupling constant k and polymer length N is studied via two state approximation. We find that the response of signal to the background noise strength is significant at optimum values of D_{opt} , k_{opt} and N_{opt} which suggests novel means of manipulating proteins or vesicles. Furthermore, the thermally activated barrier crossing rate r_k for the flexible polymer chain is studied. We find that the crossing rate r_k exhibits an optimal value at an optimal coupling constant k_{opt} ; k_{opt} decreases with N . As the chain length N increases, the escape rate for the center of mass r_k monotonously decreases. On the other hand, the crossing rate for the portion of polymer segment r_s increases and saturates to a constant rate as N steps up.

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1 Introduction

Understanding the physics of thermally activated barrier crossing for systems consisting of one or more than one degree of freedoms [1, 2, 3, 4, 5, 6, 7, 8] is ubiquitous in many scientific disciplines. It has diverse physical applications and serves as a tool to understand stochastic paradigms such as stochastic resonance and thermal ratchets. Furthermore, for bistable systems, applying fields such as an external load or nonuniform temperature breaks their symmetry along the reaction coordinate which may result in a unidirectional motion of particles. In the last few decades several model systems, which are far from equilibrium, have been proposed [9, 10]. Especially when the external load (force) varies in time, coordination of the noise with time varying force may lead to the phenomenon of stochastic resonance (SR) [11, 12] as long as the system is exposed to weak sinusoidal signals.

The phenomenon of stochastic resonance (SR) is of interest these days because of its significant practical applications in a wide range of fields. SR depicts the phenomenon that systems, by utilizing the thermal background noise, enhance their performance when they are subjected to a small periodic signal. Since the pioneering work of Benzi. *et.al* [11], the idea of stochastic resonance has been broadened and implemented in many model systems [12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. Recently the appearance of entropic stochastic resonance for a Brownian particle in a confined system has been reported in the work [22]. Unlike conventional energetic potential, the effective potential of the confined systems may have an entropic nature due to the constrained regions. For tiny-scaled biological systems that frequently exist in a highly confined geometry, the entropic contribution to the effective potential is unavoidable and plays an important role in noise-induced resonant effects.

Often biological and soft matter systems such as polymers and membranes are complex and consist of several components. Their flexibility and connectivity lead to a fascinating dynamics under certain time varying external fields and noisy environment. The resonance behavior of these systems relies not only on the strength of the background temperature, but also on their size, flexibility and shape of the potential. Thus, the interplay between the shape of the potential, flexibility and size of polymer (protein) plays a crucial role in the enhancement of signal to noise ratio SNR or spectral amplification η as reported in the works [15, 16, 17, 23].

Earlier, Lindner *et. al.* considered linearly coupled damped bistable os-

illators [15]. The dependence of SNR on the coupling strength k , number of oscillators N and noise intensity D was envisioned numerically. It has been shown that the SNR of the oscillators depicts a global maximum (SNR_{max}) at certain D and k_{opt} for a given N . Latter, utilizing Φ_4 field theory, Marchesoni *et.al* [16] independently checked the numerical results of Lindner *et. al* [15] in large N limit. Recently, Dikshtein *et.al* [17] considered a polymer in a symmetric bistable potential where the two end points of the polymer are restricted by motionless pinning points in the perpendicular direction to the symmetric potential. It has been shown that the SNR is enhanced for wider (less deep potential). More recently we studied the stochastic resonance (SR) for a flexible polymer surmounting a bistable potential. Our analysis indicated that, due to the flexibility that can enhance crossing rate and change chain conformations at the barrier, the power amplification exhibits an optimal value at optimal chain lengths N_{opt} and elastic constants k_{opt} as well as at optimal noise strengths D [23].

The study of thermally activated escape rate of polymer has been also the subject of many studies (see for example [24]). Since polymer is a flexible and an extended object with a finite length, its rate or SNR relies on its coupling constant, chain length, shape of the potential and initial conformation along the reaction coordinate in a complicated manner. Thus, more studies are needed to understand its complex dynamics. Most of the previous studies considered the center of mass motion. However, in this paper not only we examine the crossing rate for the center of mass motion r_k but also the rate for a portion of the polymer segment r_s . We find that $r_k < r_s$.

The aim of this paper is to explore the crossing rate and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential as a function of k , N and D by considering initially coiled chain conformation. First we explore the escape rate of the chain as a function of the model parameters. We show that r_k monotonously decreases with N ; the rate r_s increases and saturates to a constant value when N steps up. Since the co-operation between the monomers increases with k , the rate increases as k goes up. At certain k_{opt} , r_k attains an optimal value and further increases in k results in a lower rate as rigid polymer crosses the barrier at the expense of higher thermal kicks.

In this paper, utilizing two state approximation, the dependence of SNR on D , k and N is examined. For globular polymer chain we show the response of signal to the background noise strength is significant at optimum values of D_{opt} and N_{opt} which suggests novel means of manipulating (such as efficient

separation methods) not only for biopolymers, but also for proteins (vesicles) of different size. For the chain with a finite coupling constant k , the SNR exhibits an optimal value at an optimal k_{opt} . The signal to noise ratio for the center of mass motion SNR_k exhibits an optimal value at an optimum N_{opt} . On the other hand, the SNR_s for the polymer segment monotonously increases with N . In addition, considering temperature dependent coupling constant (entropic chain) where the elastic constant is given by $k = 3D/l^2$, we further confirm that SNR for entropic chain shows a broader and a higher peak than a chain with temperature independent coupling constant. Here, l designates the Kuhn segment length.

At this point we stress that even though the model and its numerical approach is completely different from our previous work [23], the results of this work agree with that of the previous work at least qualitatively. One can note that the dynamics of such a system can be realized experimentally. One

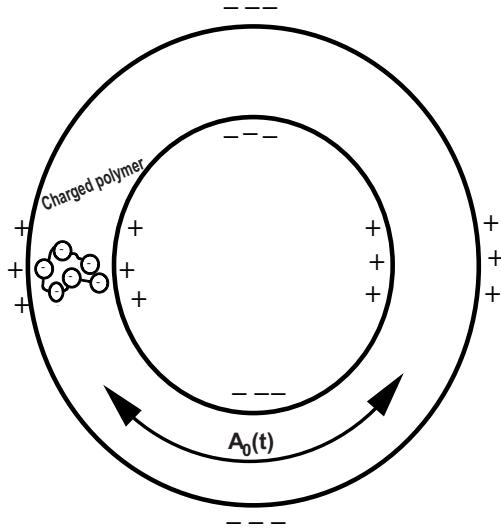


Figure 1: Schematic diagram for initially coiled polymer chain in a locally charged channel. The fluidic channel is subjected to an external periodic red force $A_0(t)$ (AC field).

makes negatively charged coiled polymer chain, then put the polymer within positively and negatively charged fluidic channel as shown in Fig. 1. The fluidic channel is subjected to an external periodic force (AC field). Since the polymer is negatively charged, it encounters a difficulty of crossing through

the negatively charged part of the channel. Assisted by the thermal background kicks along with its conformational change, the polymer ultimately overcomes the barrier. The presence of time varying force, may further enhance the rate of crossing. One can sort or manipulate polymer of specific coupling constant or chain length by tuning the angular frequency.

The rest of the paper is organized as follows: in Section 2, we present the model. In Section 3, we study the dependence of the crossing rate on the model parameters. In section 4, we discuss how the *SNR* for the flexible chain behaves as a function of the model parameters. Section 5 deals with summary and conclusion.

2 The Model

Let us now consider a flexible polymer chain of size N which undergoes a Brownian motion in one dimensional piecewise linear bistable potential as shown in Fig. 1. Considering only nearest-neighbor interaction between the polymer segments (the bead spring model), the Langevin equation that governs the dynamics of the N beads ($n=1,2,3 \dots N$) in a highly viscous medium under the influence of external potential $U(x)$ is given by

$$\gamma \frac{dx_n}{dt} = -k(2x_n - x_{n-1} - x_{n+1}) - \frac{\partial U(x_n)}{\partial x_n} + \xi_n(t) \quad (1)$$

where the k is the spring (elastic) constant of the chain while γ denotes the friction coefficient. $\xi_n(t)$ is assumed to be Gaussian white noise satisfying

$$\langle \xi_n(t) \rangle = 0, \quad \langle \xi_n(t) \xi_n(t + \tau) \rangle = 2D\gamma\delta(\tau) \quad (2)$$

with $D = k_B T$ is the strength of the thermal noise. The external potential each bead experiences is considered to be a piecewise linear potential

$$U(x) = \begin{cases} U_0\left[\frac{-x}{L_0} - 1\right], & \text{if } x \leq -L_0; \\ U_0\left[\frac{x}{L_0} + 1\right], & \text{if } -L_0 \leq x \leq 0; \\ U_0\left[\frac{-x}{L_0} + 1\right], & \text{if } 0 \leq x \leq L_0; \\ U_0\left[\frac{x}{L_0} - 1\right], & \text{if } x \geq L_0; \end{cases} \quad (3)$$

where U_0 and $2L_0$ denote the barrier height and the width of the piecewise linear bistable potential, respectively. If one considers only the center of mass motion, the second term in Eq. (1) vanishes. For a globular polymer chain,

where the coupling (spring) constant k is infinity, the Langevin equation (Eq. (1)) for the center of mass (cm) takes a simple form

$$N\gamma \frac{dx_{cm}}{dt} = \begin{cases} N\frac{U_0}{L_0} + \xi(t), & \text{if } x \leq -L_0; \\ -N\frac{U_0}{L_0} + \xi(t), & \text{if } -L_0 < x \leq 0; \\ N\frac{U_0}{L_0} + \xi(t), & \text{if } 0 < x \leq L_0; \\ -N\frac{U_0}{L_0} + \xi(t), & \text{if } x > L_0. \end{cases} \quad (4)$$

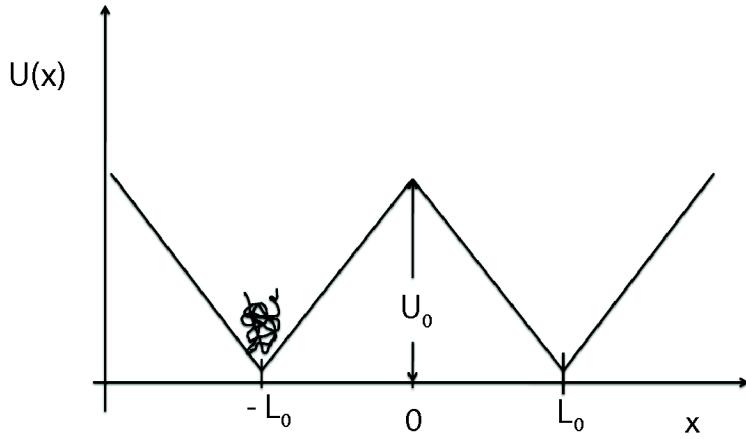


Figure 2: Schematic diagram for initially coiled polymer chain in a piecewise linear bistable potential. The potential wells and the barrier top are located at $x = \pm L_0$ and $x = 0$, respectively. Due to the thermal background kicks, the polymer ultimately crosses the barrier assisted by its conformational change along the reaction coordinate.

3 Polymer escape rate

We consider a polymer which has initially coiled conformation along the piecewise linear bistable potential as shown in Fig. 2. Due to the thermal background kicks, the polymer presumably crosses the barrier. The crossing rate of the chain strictly relies on the chain length, coupling constant, barrier height and noise strength. For a compact polymer ($k \rightarrow \infty$), the monomers feel the same force along the reaction coordinate (see Eq. (4))

and due to lack of chain conformational change at the top of the barrier, its escape rate is considerably lower than a polymer of finite k value. On the other hand, the jumping rate also depends on the choice of coordinate system. The rate for the center of mass motion is a decreasing function of N while the escape rate for the portion of polymer segment increases with N . The thermally activated rate strictly relies on the chain initial conformation along the piecewise linear bistable potential for the case where the microscopic relaxation time of the polymer is significant compared to the crossing time. In this case, initially stretched polymer crosses the barrier faster than coiled chain. This is because coiled polymer first stretches before crossing the barrier. The degree of stretching depends on the relaxation time of the polymer which itself relies on the chain length, coupling constant and the thermal background kicks. For short polymer chain surmounting a potential barrier that is large compared to D , $NU_B \gg D$, the chain crossing time is considerably larger than its relaxation time and hence the crossing time may be independent of chains initial conformation. The activated barrier crossing considered in this work strictly applicable only to the case where the crossing time is much larger than any microscopic relaxation times of the polymer.

Before we discuss how the flexible polymer chain in the double-well potential behaves, let us first calculate the crossing rate for a globular polymer chain. The problem of surmounting a piecewise linear bistable potential for a single Brownian particle in high friction limit was addressed in the work [26]. Following the same approach, the mean first passage time MFPT for the compact polymer crossing over a high potential barrier is given by

$$MFPT = \frac{\gamma}{D} \left(\frac{DL_0}{NU_0} \right)^2 e^{\frac{NU_0}{D}} \quad (5)$$

while the crossing rate

$$r_k = \frac{D}{\gamma} \left(\frac{NU_0}{DL_0} \right)^2 e^{\frac{-NU_0}{D}} \quad (6)$$

is the inverse of MFPT. The dependence of the crossing rate r_k or equivalently the $MFPT$ on the potential height U_0 , width of the potential $2L_0$ and chain length N can be analyzed by exploiting Eq. (6). When U_0 increases, the polymer encounters a difficulty of jumping the piecewise linear bistable potential and as a result r_k declines. When N increases, r_k decreases as large polymer crosses the potential barrier at the expense of higher thermal kicks.

On the other hand, as L_0 steps up, the *MFPT* for the polymer to reach to the other side of the well increases which implies r_k monotonously decreases.

For the chain with a finite coupling constant, we analyze the crossing rate via numerical simulation. We introduce dimensionless parameters: $\bar{x} = x/L_0$, $\tau = \gamma L^2/U_0$, $\bar{k} = kL^2/U_0$ and $\bar{t} = t/\tau$. Hereafter all the quantities are rescaled (dimensionless) so the bars will be dropped. The behavior of the system is analyzed by integrating the Langevin equation (1) (employing Brownian dynamics simulation). In the simulation, coiled polymer chain with N monomers is initially situated in one of the potential wells. Then the trajectories for the center of mass of the polymer or the portion of polymer segment is simulated by considering different time steps Δt and time length t_{max} . In order to ensure the numerical accuracy, up to 5×10^5 ensemble averages have been obtained.

Let us now vary the rescaled spring constant k of the chain. Figure 3 plots the dependence of r_k on the rescaled k for parameter choice $N = 10$, $N = 20$, $N = 25$ and $D = 0.5$. For small k , since the monomers become non-interacting (non-cooperative), r_k tends to be smaller. When coupling strength between the monomers k further increases, the tendency for interconnected monomers to assist each other increases as a result r_k steps up. At certain optimal k_{opt} , r_k attains an optimum value. Further increasing in k results in a lower crossing rate as larger thermal energy is required to drive the rigid chain across the reaction coordinate. The same figure depicts that k_{opt} is a decreasing function of N . The coupling constant k_{opt} relies on rescaled noise strength D in a manner $k = 3DL^2/l^2$. The crossing rate for this entropic chain has been analyzed and compared with the chain of a finite k . The numerical analysis shows the rate for entropic chain is considerably higher; further details will be reported elsewhere.

Figure 4a depicts the plot of r_k as a function of N for parameter choice $D = 0.25$, $D = 0.6$ and $k = 0.5$. The crossing rate for the center of mass motion monotonously decreases with N . On the contrary, the rate of the polymer segment r_s increases and saturates to a constant value as N and D step up as shown in Fig. 4b.

4 Stochastic resonance

In the presence of time varying signal, the interplay between noise, sinusoidal driving force together with chain flexibility and chain length in the bistable

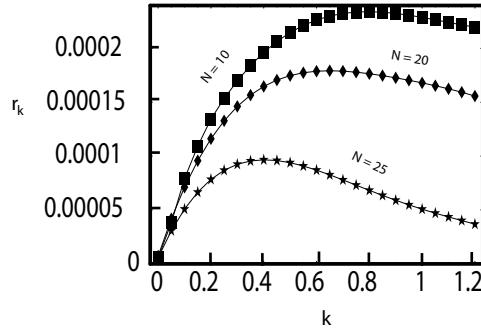


Figure 3: Polymers crossing rate r_k as a function of coupling constant k for different chain length N and noise strength $D = 0.5$. The simulation results are obtained directly by integrating Eq. (1). The figure exhibits that the rate increases as N declines and attains an optimal value at an optimal elastic constant k_{opt} . The optimal coupling constant shifts to the right as N decreases.

system may lead the system into stochastic resonance provided the random tracks are adjusted in an optimal way to the recurring external force. Next we study the dependence of the SR on the model parameters employing two state approximations without considering a continuous diffusion dynamics.

In the presence of a periodic signal $A_0 \cos(\Omega t)$, the Langevin equation that governs the dynamics of the system is given by

$$\gamma \frac{dx_n}{dt} = -k(2x_n - x_{n-1} - x_{n+1}) - \frac{\partial U(x_n)}{\partial x_n} + A_0 \cos(\Omega t) + \xi_n(t) \quad (7)$$

where A_0 and Ω are the amplitude and angular frequency, respectively.

Employing two state model approach [12, 25], two discrete states $x(t) =$

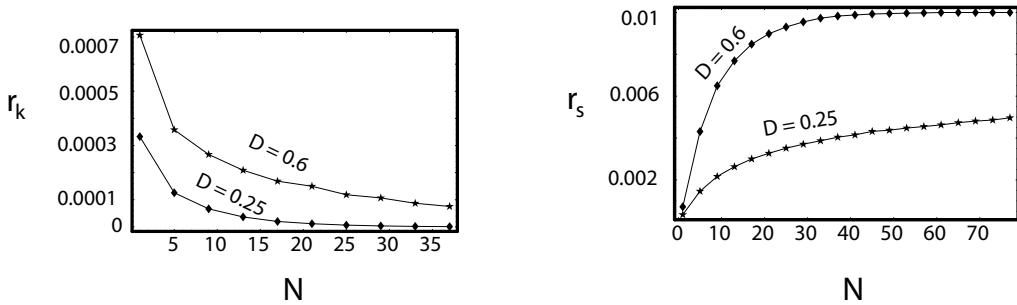


Figure 4: (a) Dimensionless rate r_k versus N . (b) The escape rate for polymer segment r_s versus N . The data are obtained numerically for different rescaled noise strength D and coupling constant $k = 0.5$.

$\pm L_0$ are considered. Let us denote n_+ and n_- to be the probability to find the polymer segment in the right (L_0) and in the left ($-L_0$) sides of the potential wells, respectively. In the presence time varying signal, the master equation that governs the time evolution of n_{\pm} is given by

$$\dot{n}_{\pm}(t) = -W_{\pm}(t)n_{\pm} + W_{\mp}(t)n_{\mp} \quad (8)$$

where $W_+(t)$ and $W_-(t)$ corresponds to the time dependent transition probability towards the right (L_0) and the left ($-L_0$) sides of the potential wells. The time dependant rate [12, 25] takes a simple form

$$W_{\pm} = r_k \exp \left[\pm \frac{L_0 N}{U_0 D} A_0 \cos(\Omega t) \right] \quad (9)$$

where r_k is the Kramers rate for the polymer in the absence of periodic force $A_0 = 0$. We consider the case where $N \gg D$. For sufficiently small amplitude, one finds the signal to noise ratio

$$SNR = \pi r_k \left(\frac{A_0 N L_0}{U_0 D} \right)^2. \quad (10)$$

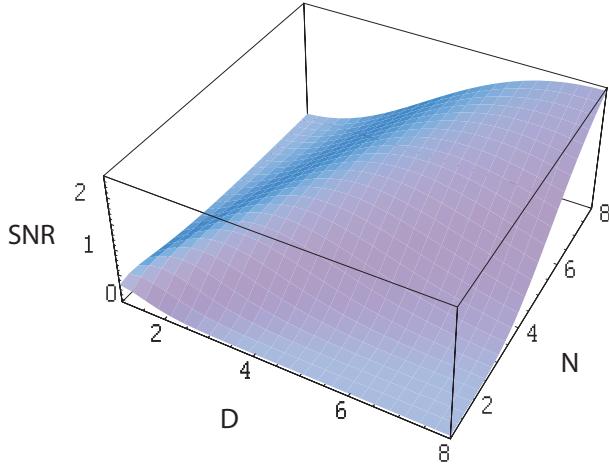


Figure 5: (Color online) The dependence of $SNR \times 10^{-6}$ (for compact polymer chain) on N and D for parameter choice $A_0 = 0.05$. The SNR is obtained via Eqs. (6) and (10).

Before we explore how the SNR for globular polymer behaves as a function of N , we introduce additional dimensionless parameter: $\bar{A}_0 = A_0 L / U_0$. From now on for convenience the bar will be dropped. Figure 5 depicts the plot for the SNR for a globular polymer chain versus D and N for fixed values of the driving frequency and potential width. The SNR exhibits non-monotonic noise strength dependence revealing a peak at an optimal noise strength D_{opt} . D_{opt} steps up as N inclines. This is because longer polymer crosses the barrier at the expense of higher thermal excitation. The same figure exhibits that the SNR peaks at optimum chain length N_{opt} . This suggests novel means of manipulating not only for biopolymers, but also for proteins (vesicles) of different size. One can note that since compact polymer lacks the flexibility to conform to the piecewise linear bistable potential, the peak of the SNR is less than that of a flexible polymer chain.

For the chain with a finite coupling constant k , the resonance behavior of the system is examined numerically. Figure 6 shows the plot for the SNR_k as a function of k for different values of N . Other parameters are fixed as $D = 0.25$ and $A = 0.1$. For small k , the monomers tend to be non-interacting as a result the SNR becomes very small. The SNR peaks at an optimal chain length k_{opt} and further increasing in k leads again to a smaller SNR as the rigid polymer is not flexible enough to adjust itself with the time varying

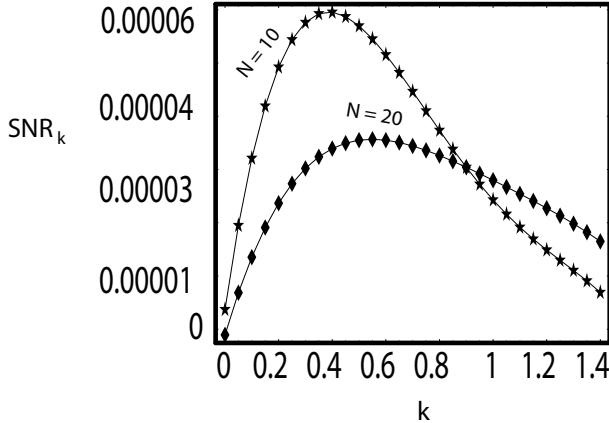


Figure 6: The dependence of SNR_k as a function of coupling constant k for different chain length N , for noise strength $D = 0.25$ and amplitude $A_0 = 0.1$. The simulation results are obtained directly by integrating Eq. (1). The figure exhibits that the SNR increases as N declines and attains an optimal value at an optimal elastic constant k_{opt} . Unlike the corresponding rate, the optimal coupling constant shifts to the left as N decreases.

force. The optimal spring constant k_{opt} increases as N increases.

Figure 7a plots the rate SNR_k versus N . We observe an increase in the signal to noise ratio when the number of monomers increases. The SNR peaks at an optimal chain length N_{opt} and declines again as the chain length increases. On the contrary, SNR_s monotonously increases with N (see Fig. 7b). It is worth noting that since the flexible polymer chain responds in more cooperative and coherent manner to the time varying force, it exhibits a higher resonance peak than a globular polymer.

Finally we emphasize that even though the model and its numerical approach is completely different from our previous work [23], the results agree with that of the previous work at least qualitatively. For instance, similar to this work, in our previous work we found that the response of signal to the background noise strength is significant at optimum values of D_{opt} , K_{opt} and N_{opt} . Our previous work [23] dealt with the study of SR for a flexible polymer chain on Kramers potential. Depending on the chain length N and spring constant k , the chain takes either coiled or stretched conformation at the top of the barrier. When the chain is either in coiled or stretched state, the resonance is much larger than globular state revealing the intrinsic flex-

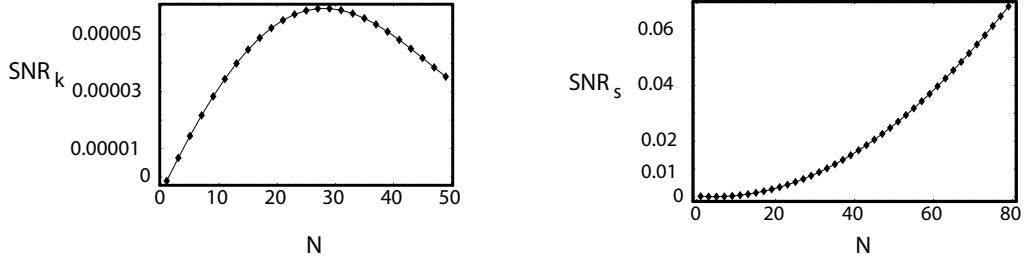


Figure 7: (a) SNR_k versus N . (b) SNR_s for polymer segment as a function of N . The data are obtained numerically for noise strength $D = 0.5$, amplitude $A_0 = 0.1$ and coupling constant $k = 0.5$.

ibility of the chain facilitating faster crossing. In the globular limit $k \rightarrow \infty$, the resonance becomes small as the compact polymer lacks the flexibility to conform to the driving force. Furthermore, we showed that the power amplification peaks at an optimal chain length and elastic constant as well as at an optimal noise strength.

5 Summary and conclusion

In summary, in this work we explore the crossing rate and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential. We investigate the chain's escape rate as a function of different model parameters. r_k monotonously decreases with N while the rate r_s increases and saturates to a constant rate when N steps up. Due to lack of cooperation between the monomers, the rate is considerably small for a smaller k . The crossing rate increases as k goes up. At certain k_{opt} , r_k attains an optimal value. Further increasing in k results in a lower rate as rigid polymer crosses the barrier at the expense of higher thermal kicks.

Employing two state approximation, the dependence of SNR as a function of model parameters is studied. For a globular polymer chain we show the response of signal to the background noise strength is significant at optimum values of D_{opt} and N_{opt} which suggests novel means of manipulating proteins (vesicles) of different size. On the other hand, for the chain with a finite coupling constant k , the SNR exhibits an optimal value at an optimal k_{opt} . The signal to noise ratio for the center of mass SNR_k exhibits an optimal value at an optimum N_{opt} . The SNR for the polymer segment SNR_s

monotonously increases with N .

In conclusion, in this work, by introducing a different model system than the previous work [23], we recapture the previous results at least qualitatively. Not only we assess the resonance property of the system, but we also further explore the barrier crossing rate by varying different model parameters. Since polymers are interconnected and flexible systems, they exhibit interesting cooperative dynamics when they are exposed to time varying external fields and noises. Understanding their dynamics is crucial not only for novel means of manipulating proteins such as DNA or RNA molecules in a nanofluidic or microfluidic channels, but also to understand how such systems self-organize their flexible degrees of freedom. Thus, this theoretical study is crucial not only for the fundamental understanding of polymer physics, but also provides a basic paradigm in which to understand the self-organization and cooperativity induced by the chain flexibility and fluctuations.

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